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Dynamic smoothing of nanocomposite films

Y. T. Pei,[1,a)] A. A. Turkin,[2] C. Q. Chen,[1] K. P. Shaha,[1] D. Vainshtein,[1] and J. Th. M. De Hosson[1]
[1]*Department of Applied Physics, Materials Innovation Institute (M2i), University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[2]*National Science Center "Kharkov Institute of Physics & Technology", 1 Akademicheskaya str., UA-61108 Kharkov, Ukraine*

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In contrast to the commonly observed dynamic roughening in film growth we have observed dynamic smoothing in the growth of diamondlike-carbon nanocomposite (TiC/a-C) films up to 1.5 μm thickness. Analytical and numerical simulations, based on the Edwards–Wilkinson model and the Mullins model, visualize the effect of the diffusivity parameters and the noise strength on the interface evolution of dynamic smoothing. The prediction is in a good agreement with the measured roughness evolution. High-resolution transmission electron microscopy shows that the formation of an amorphous front layer 2 nm thick excludes possible influence of nanocrystallites on the dynamic growth behavior of the nanocomposite film. © *2010 American Institute of Physics*. [doi:10.1063/1.3394019]

Making a smooth low-friction surface is an epitome in materials design. This is so because roughness over various length-scales determines the overall response. Further, roughness may have a crucial influence on the attachment and detachment of layers from a substrate. This topic was studied initially by Fuller and Tabor,[1] and it was shown that a relatively small surface roughness could diminish or even remove the adhesion. In their model a Gaussian distribution of asperity heights was considered with asperities having all the same radius of curvature. On the other hand, randomly rough surfaces, which are commonly encountered for solid surfaces, possess roughness over many different length scales rather than a single one.[2] The overarching challenge is, therefore, the design of a surface layer that is free of roughness that degrades the structural and functional behavior.

Unfortunately manufacturing processes of hard and frictionless films lead to roughening of the outer surface. Dynamic roughening is a common phenomenon observed in plasma processing of materials, including both film deposition and plasma etching, that is to say, the roughness of a growing/etching interface increases with process time. As a result in film deposition, a rough interface induces columnar growth that is undesired because the column boundaries are the source of potential failures of various modes, e.g., by cracking and corrosion. In contrast, ultrasmooth interfaces allow growing pinhole-free films of only 1–2 nm thickness, which is very important technologically, for instance in magnetic disk storage systems.[3] In view of this consequence, during the past two decades considerable effort has been devoted to the experimental investigation and theoretical simulation of the roughness evolution of growing interfaces.[4–8]

Recently, we have demonstrated the controlled transition from dynamic roughening into a dynamic smoothing regime in film growth.[9] In this paper, the interface profile of growing films has been numerically simulated to visualize the effect of the diffusivity parameters and the noise strength on the interface evolution of dynamic smoothing, importantly not in thin amorphous but in thick nanocomposite films composed of crystalline nanoparticles and amorphous carbon matrix.

Diamondlike-carbon based nanocomposite (TiC/a-C) films were deposited on Si-wafer with nonreactive magnetron sputtering in a closed-field unbalanced magnetron sputtering system. The detailed setup has been described elsewhere.[10] It consisted of four magnetrons coupled to one Ti and one Cr target powered by a double channel dc power supply and two graphite targets opposite to each other powered by a double channel pulsed-dc (p-dc) power supply operating at 350 kHz and 60% duty cycle. The substrates located at 80 mm distant from the targets were biased at -40 V by p-dc operating at 250 kHz and 87.5% duty cycle. A CrTi interlayer of 200 nm thickness was first deposited to enhance interfacial adhesion. Thereafter, the TiC/a-C top film was deposited under the condition of 1.5 A sputtering current applied to each of the two graphite targets and 0.5 A current to the single titanium target, at an averaged growth rate of 0.10 $\mathrm{nm\,s^{-1}}$ for different deposition times, from 7.5 min up to 4 h. The energy and flux density of impinging Ar^+ ions on the growing film was $1.3\times10^{15}\ \mathrm{eV\,s^{-1}\,cm^{-1}}$ and $2\times10^{13}\ \mathrm{s^{-1}\,cm^{-1}}$, respectively, measured with an EQP300 plasma analyzer (Hiden Analytical Ltd., U.K.).

A Digital Instrument NanoScope IIIa and Dimension 3100 atomic force microscope (AFM) with a Si tip of nominal 10 nm radius were used to probe the surface morphology of the deposited films. The nanostructure of the films was revealed with high resolution transmission electron microscopy (HRTEM) using JEOL 2010-FEG.

The roughness evolution of TiC/a-C films versus deposition time measured with AFM is shown in Fig. 1, continuously decreasing from 0.30 nm at 10 s to 0.23 nm at 4 h deposition time. From the log-log plot, one obtains an average growth exponent of -0.076, clearly pointing to a growth regime of dynamic smoothing. The analysis of surface topography (AFM images) in terms of the power spectral density indicates that the dynamic smoothing of the interfaces can be described by the equation containing the Edwards–Wilkinson term $D_2\nabla^2(\ldots)$ and the Mullins term $D_4\nabla^2[\nabla^2(\ldots)]$,[11,12] as follows:

a)Electronic mail: y.pei@rug.nl.

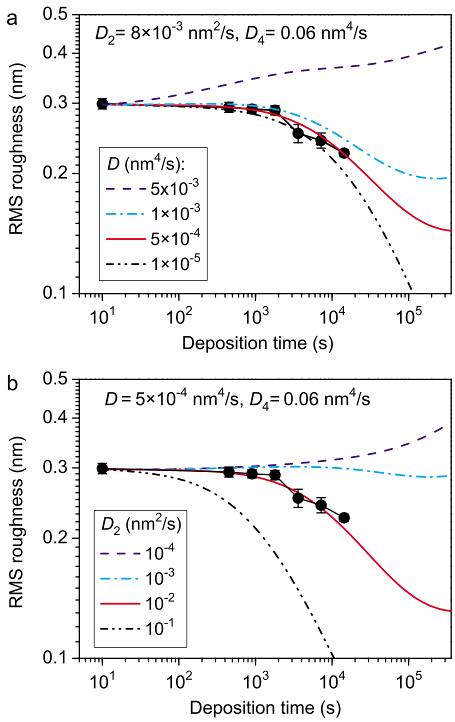

FIG. 1. (Color online) Time dependence of the interface roughness of TiC/a-C films: (a) the influence of the noise strength D and (b) the effect of the diffusion coefficient D_2 responsible for the downhill flow of adatoms induced by the concurrent Ar^+ ions impingement. The model curves are found from the solution of Eqs. (1)–(3). The black curve of round symbols is the experimental result.

$$\frac{\partial h(\mathbf{r},t)}{\partial t} = D_2\nabla^2 h(\mathbf{r},t) - D_4\nabla^2[\nabla^2 h(\mathbf{r},t)] + \eta(\mathbf{r},t), \qquad (1)$$

with $h(\mathbf{r},0)=h_0(\mathbf{r})$, where $h(\mathbf{r},t)$ is the deviation of the two-dimensional interface profile $Z(\mathbf{r},t)$ from its middle plane of a growing film with a mean thickness $\langle Z(\mathbf{r},t)\rangle = Ft$ and $h_0(\mathbf{r})$ is the initial profile of CrTi interlayer. F is the mean deposition rate. Local fluctuations of the deposition flux are taken into account by the term $\eta(\mathbf{r},t)$ which is assumed to be the space-time white noise with zero mean, as follows:

$$\langle \eta(\mathbf{r},t)\eta(\mathbf{r}',t')\rangle = D\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \qquad (2)$$

where angular brackets stand for the averaging over noise and $\delta(\ldots)$ is the two-dimensional (2D) delta-function. It can be shown that the noise strength D is proportional to the deposition flux.[13] D_2 and D_4 are positive diffusivity parameters that control the atomic mobility along the interface. The physical mechanisms controlling the diffusivities D_2 and D_4 are discussed in detail elsewhere.[14] Here we mention in particular the mechanism responsible for the diffusion coefficient D_2, namely, the downhill flow of subsurface atoms resulting from displacements of atoms by energetic Ar^+ ions.[4]

The formal solution to Eq. (1) can be written as,

$$h(\mathbf{r},t) = \Im^{-1}\{\Im[h_0(\mathbf{r})]e^{-a(q)t}\} + \Im^{-1}\left\{\int_0^t \Im[\eta(\mathbf{r},t')]e^{-a(q)(t-t')}dt'\right\}, \qquad (3)$$

where $a(q)=D_2q^2+D_4q^4$, $\mathbf{q}$ is the vector in 2D reciprocal space. $\Im$ and $\Im^{-1}$ stand for the direct and inverse Fourier transforms, respectively. Note that the first term decreases with time, i.e., the contribution from the initial profile ceases with deposition time or film thickness.

The time dependence of statistical properties of the growing interface—the rms roughness and the correlation function—can be found without detailed knowledge of interface evolution, e.g., by the technique of the power spectrum distribution via Fourier analysis.[15] The dependence of the rms roughness on the model parameters along with the experimentally measured roughness is shown in Fig. 1. At a given "smoothing efficiency" D_2 and D_4, the interface roughness decreases significantly with the deposition time but may also increase upon time once the deposition flux is beyond a threshold [Fig. 1(a)]. Therefore the deposition flux comes into play mainly at high growth rates where dynamic roughening is observed. Figure 1(b) shows the influence of the diffusivity parameter D_2 on the time dependence of interface roughness. It is noteworthy that variation in D_2 can affect considerably the dynamic behavior of interface roughening/smoothing and the prediction for a long deposition time is in a good agreement with the experiments. On the other hand, the gradient of chemical potential along the interface and the local temperature increase due to the energy delivered to the growing interface by impinging Ar^+ ions may also lead to interface smoothing by means of surface diffusion through the coefficient D_4, which has only a minor effect in comparison with D_2 according to our simulation.[14] That is to say, the smoothing process is governed by the second order Edwards–Wilkinson term on length scales larger than the critical length scale $L^*=\sqrt{D_4/D_2}$ (a couple of nanometer for the simulated cases in Fig. 1), and the fourth derivative term becomes dominant only on scales smaller than L^*.

To visualize the effect of the diffusivity parameters and the noise strength on the interface evolution, we have simulated the interface profiles of the growing film by numerical evaluation of the Eq. (3) on a 512×512 lattice (i.e., 2000×2000 nm^2 area). The deposition noise $\eta_{nm}^{\alpha} = \sqrt{D/(\Delta x^2\Delta t)}\xi_{nm}^{\alpha}$ has been generated at the lattice points (x_n,y_m) (Δx is the spacing between points) at all time moments $t\le t_\alpha$ with a time increment Δt. The random numbers ξ_{nm}^{α} are taken from the Gaussian distribution with mean zero and unit variance. The "discrete" deposition noise η_{nm}^{α} has the same variance as the spatial average of the continuous noise $\eta(\mathbf{r},t)$ on the square area Δx^2 around (x_n,y_m) integrated over the time interval Δt.[16] The initial interface $h_0(\mathbf{r})$ has been extracted from the AFM micrograph and then Eq. (3) is integrated numerically. The results are presented in Fig. 2, where each figure demonstrates the sensitivity of the interface profile and roughness to a variation in the parameters D, D_2, and D_4, respectively. The results of the numerical simulation clearly confirm that both smoothing and roughening are observed depending on noise strength D [Figs. 2(a) and 2(b)]. At a fixed deposition rate or noise strength D, the coefficient D_2 of the second order Edwards–Wilkinson term controls the smoothing process of the low-frequency or large-scale interface undulations [Figs. 2(a), 2(c), and 2(d)], whereas the coefficient D_4 of the Mullins term is responsible for the high-frequency or small-scale undulations (see Figs. 2(a), 2(e), and 2(f)).

Although very low roughness and $\beta\sim0$ had been observed in ta-C amorphous thin films (~70 nm thickness),[5] we report here the dynamic smoothing effect in much thicker films (up to 1.5 μm thickness), revealing a more general

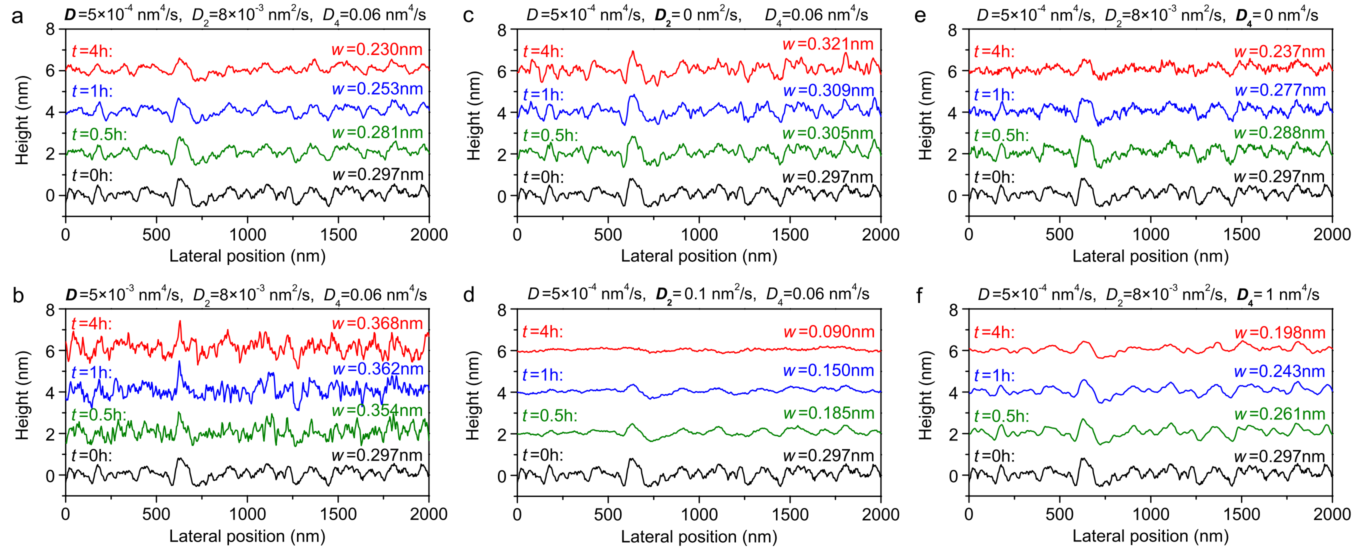

FIG. 2. (Color online) Numerically simulated interface profiles vs deposition time (t), with the interfaces roughness (w) indicated: (a) profiles simulated with the basic set of parameters to fit the experimental result plotted in Fig. 1; (b) with high deposition noise; (c) with no D_2 diffusion; (d) with high value of D_2 diffusivity; (e) with no D_4 diffusion, and (f) with high value of D_4 diffusivity. For clarity, each profile is shifted along z-axis by 2 nm.

phenomenon of dynamic smoothing of growing interfaces induced by concurrent Ar^+ ion impingement. Especially, the dynamic smoothing is active in a film consisting of nanocrystalline phases of sizes one order of magnitude larger than the surface roughness. Therefore, verification of the growth mode of nanocomposite films is crucial in the study of their dynamic smoothing behavior, in terms of whether the nanocrystallites are formed directly on the interface or underneath in relation to the evolution of interface profile. The cross-sectional HRTEM micrograph in Fig. 3 reveals a purely amorphous front layer of about 2 nm thickness, which covers the bulk nanocomposite film. The TiC nanocrystallites form only underneath this amorphous front layer. It is considered that the concurrent Ar^+ ions impingement of high energy flux induces the formation of the amorphous front layer. This observation supports the subplantation model[17,18] and the downhill flow model,[4] where amorphousness is the prerequisite. Such an amorphous front layer excludes any influence of nanocrystallites on the dynamic growth behavior of the nanocomposite films.

In summary, we have shown dynamic smoothing of growing interface in thick TiC/a-C nanocomposite films characterized by a negative growth exponent. The prediction of analytical and numerical simulations based on the Edwards–Wilkinson model and the Mullins model is in a good agreement with the experimentally measured roughness evolution. Under the condition of intensively concurrent ion impingement, the formation of an amorphous front layer is observed responsible for ultrasmoothness. The observed dynamic smoothing will affect the frictional properties to a great extent and the work provides useful generic design rules for nanocomposites thin films of ultralow friction.

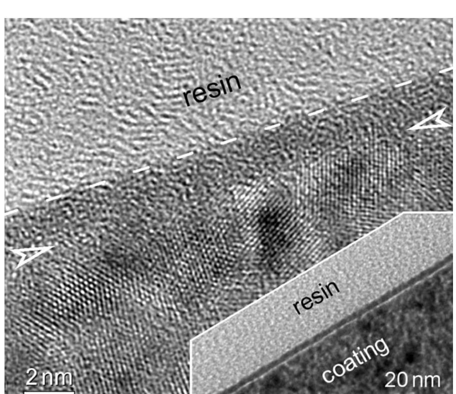

FIG. 3. Cross-sectional HRTEM micrograph of the film revealing that an amorphous front layer of about 2 nm thickness covers the bulk nanocomposite film. The inset is an overview of the growing interface.

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